PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Form PCT/IPEA/416
13324WO/mi		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2004/006115	07.06.2004	13.06.2003

International Patent Classification (IPC) or national classification and IPC
C23F1/46, C23G1/36, C25C7/00, C25C1/12

Applicant
ATOTECH DEUTSCHLAND GMBH et al.

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 3 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
10.02.2005	29.08.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Mauger, J Telephone No. +49 89 2399-8447

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/006115

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-13	as originally filed
Claims, Numbers	
1-10	received on 01.08.2005 with letter of 01.08.2005
Drawings, Sheets	
1/3-3/3	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/006115

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-10
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-10
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V.

1 The following documents are referred to in this communication:
D1 : US 3 825 484 A (FRONSMAN L ET AL) 23 July 1974 (1974-07-23)
D2 : DATABASE WPI Section Ch, Week 197649 Derwent Publications Ltd., London, GB; Class M14, AN 1976-91354X XP002294718 -&; JP 51 119632 A (CHUO KK) 20 October 1976 (1976-10-20)

2) The present application defines a method for regenerating iron-containing copper pickling or etching solutions by electrolytically depositing copper (claim 1), an apparatus for performing the method (claim 7) and a system for etching or pickling copper (claim 10).

3) Document D1, which is considered to represent the most relevant state of the art, discloses (see column 1, lines 40-57, column 2, line 65 to column 4, line 73, claims and figures) a method and apparatus for regenerating iron chloride containing copper etching baths. The method includes feeding the used etchant to a membrane and diaphragm free electrolysis cell containing a plurality of rotating cathodes and fixed inert anodes. The cathodes rotate into and out of the bath. The cell also comprises a scraper placed outside the bath for removing copper from the cathodes and deflector means for collecting this copper outside the cell. The unit is sealed by a cover.

The subject-matter of the independent claims differs from the disclosure of document D1 in that the means are provided to apply a potential to the recovered copper. The claimed subject-matter is therefore novel (Art. 33(2) PCT)

The problem to be solved by the present invention may be regarded as providing a simpler and more compact electrolysis apparatus that is easy to employ in situ.

3.1) The application of a potential to the recovered copper prevents it from redissolving and thus allows it to be directly recovered in the bath. Thus there is no need for the cathode to rotate out of the bath. This allows a simple compact bath with integrated copper recovery to be used as well as a smaller cathode. Thus the problem is solved.

The use of a potential to prevent copper redissolution is known from document D2, however this relates to a cell with a diaphragm and without a scraper.

In order for the use of a potential to prevent copper redissolution to be useful, the copper has to be recovered in the bath. Document D2 does not provide a teaching enabling a skilled person to modify the entire cathode and copper recovery structure of document D1 to enable copper to be recovered directly in the bath. Thus a combination of documents D1 and D2 does not make the claimed subject-matter obvious. Hence an inventive step can be recognised for the subject-matter of claims 1-10 (Article 33(3) PCT).

CLAIMS

1. Method for regenerating etching solutions containing iron for the use in etching or pickling copper or copper alloys, characterized by the following steps:

(i) feeding the etching solution to be regenerated from the etching system into an electrolysis cell being hermetically sealed or having an anode hood (8), the electrolysis cell comprising a cathode (1), an inert anode (2), means (3) for removing the electrolytically deposited copper from the cathode and means (4) for collecting the removed copper and applying a potential to the removed copper, wherein the electrolysis cell does not have an ion exchange membrane or a diaphragm, and wherein the etching solution to be regenerated contacts the cathode of the electrolysis cell first,

(ii) electrolytically depositing the copper comprised in the etching solution at the cathode (1),

(iii) oxidising the Fe(II) comprised in the etching solution to Fe(III) at the anode (2),

(iv) removing the copper deposited at the cathode (1),

(v) applying a potential to the removed copper to prevent re-dissolving of the copper, and

(vi) returning the etching solution being thus treated to the etching system.

2. Method according to claim 1, characterized in that the flow of the etching solution through the electrolysis cell and/or the current flowing through the electroly-

sis cell is controlled by on-line measuring the concentration of Fe(II)/Fe(III) or the concentration of Cu.

3. Method according to claim 2, characterized in that the on-line determination of the concentration of Cu is carried out by photometric methods or by potentiometric measurement.

4. Methods according to claims 1-3, characterized in that the electrolysis is carried out in the electrolysis cell using direct current.

5. Method according to claims 1-3, characterized in that the electrolysis is carried out in the electrolysis cell using pulsed current.

6. Method according to claims 1-5, characterized in that the etching solution is allowed to flow to the cathode first and subsequently to the anode.

7. Apparatus for carrying out the method according to claims 1-6, comprising a separate electrolysis cell being hermetically sealed or having an anode hood (8), the electrolysis cell having a cathode (1) and an inert anode (2), means (3) for removing the electrolytically deposited copper from the cathode, means (4) for collecting the removed copper and for applying a potential to the removed copper, an inlet (5) in the lower region of the electrolysis cell between the cathode (1) and the means (4) for collecting the removed copper and applying a potential to the removed copper and an outlet (6), wherein the electrolysis cell does not have an ion exchange membrane or a diaphragm.

8. Apparatus according to claim 7, characterized by further having valves (7) for discharging the regenerated copper.

9. Apparatus according to claim 7 or claim 8, characterized in that the cathode (1) is in the form of a rotating cathode and the means (3) is in the form of a stripping plate.

10. System for etching or pickling of work pieces comprising an apparatus according to claims 7 to 9.